Evolution of Spectral Function in a Doped Mott Insulator: Surface vs Bulk Contributions

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We study the evolution of the spectral function with progressive hole doping in a Mott insulator, $La_{1-x}Ca_xVO_3$ with $x = 0.0-0.5$. The spectral features indicate a bulk-to-surface metal-insulator transition in this system. Doping dependent changes in the bulk electronic structure are shown to be incompatible with existing theoretical predictions. An empirical description based on the single parameter U/W is shown to describe consistently the spectral evolution. [S0031-9007(98)05723-8]

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It is well understood that the insulating ground state of transition metal compounds with integral occupancies of $3d$ levels (Mott insulators) arise from strong electron correlation effects. Recent years have seen a phenomenal resurgence of interest in studying the properties of such systems doped with charge carriers representing fractional $3d$ occupancies, leading to the discovery of many exotic properties such as the high temperature superconductivity [1] and colossal magnetoresistance [2]. A considerable amount of effort has been directed to modeling these systems theoretically, which is crucial for understanding such properties. In recent times, there are very specific predictions about the evolution of the spectral functions in doped Mott insulators based on the Hubbard model in the limit of infinite dimension [3,4]. Considerably different ansatz, such as slave boson [5], dynamical mean field theories [6], and exact calculations [7] for finite systems, yield qualitatively similar results. These predictions are most useful, since the spectral function can be directly measured experimentally by photoemission spectroscopy and, thus, provide a very convenient testing ground for the suitability of the model. In order to investigate the spectral evolution as a function of doping we have studied $La_{1-x}Ca_xVO_3$ for $x = 0.0-0.5$. $LaVO_3$ is a Mott insulator with the d^2 electronic configuration. Ca substitution dopes holes into the system continuously varying the electron count from 2 to 1.5 per V ion for the compositions studied. Transport and magnetic measurements [8] have shown that the system is an antiferromagnetic insulator for $x < 0.2$, but is Pauli paramagnetic metal for $x \geq 0.2$. Moreover, there is no significant structural modification suggesting nearly constant bandwidth (W), with a little ($\leq 10\%$) change in Hubbard U across the compositions studied [9]. Hence, the change in the electronic structure in this system is driven primarily by the changes in the doping level and, thus, provide a suitable case for investigating the spectral evolution in a doped Mott insulator. We observe the surface electronic structure in this system to be considerably different from the bulk one and provide an algorithm to extract the true bulk electronic structure from the total spectra using photon energy dependence of the spectral functions. The extracted bulk spectra show that existing theories based on the Hubbard model are insufficient to describe the experimentally observed spectral functions for various dopings. We provide an empirical approach to describe the observed evolution of the spectral function and discuss the implications of our findings.

Polycrystalline samples of $La_{1-x}Ca_xVO_3$ were prepared as reported elsewhere [8], from congruently molten states giving rise to large grains with strong intergrain bonding and about 1% of impurity phases in the grain boundaries. The x-ray photoemission (XP) and ultraviolet photoemission (UP) spectroscopic measurements were carried out at liquid nitrogen temperature in a vacuum of 4×10^{-10} mbar with resolutions of 0.8 and 0.08 eV, respectively. The cleanliness of the sample surface was maintained by periodical scraping with an alumina file *in situ* and was monitored by O $1s$ and C $1s$ spectral regions in XP and the characteristic region (9–12 eV binding energy) in UP measurements. Reproducibility of the spectra with repeated scrapings was confirmed for each composition. We believe that the spectra are representative of angle integrated spectra, since they are obtained over a wide ($\pm 10°$) acceptance angle and were always independent of sample rotation about the surface normal. The bulk spectra were extracted primarily from the XP spectra, which, by their nature, average over a large part of the Brillouin zone. We implicitly assume that the incident photon energy-dependent cross sections and the combined resolution do not seriously change the spectra over our narrow (3 eV) binding energy window; we substantiated this assumption explicitly for $LaVO_3$. The derived spectra for the bulk, within our resolution and over the relatively large energy range investigated here, are not affected by the disorder due to scraping. The bulk and surface compositions were found to be in agreement with nominal compositions from energy dispersive x-ray analysis and the intensity ratio of the core level spectra of the components, respectively.

In Fig. 1 we show the He I UP spectra for all the compounds near the V $3d$ emission region. Each spectrum is dominated by a feature centered at about 1.5 eV below E_F, with no intensity at the Fermi level (E_F) for $x = 0.0$ and 0.1. This feature is normally termed as an incoherent feature [10] being the spectral signature of the lower Hubbard band (LHB) and corresponds to electron states

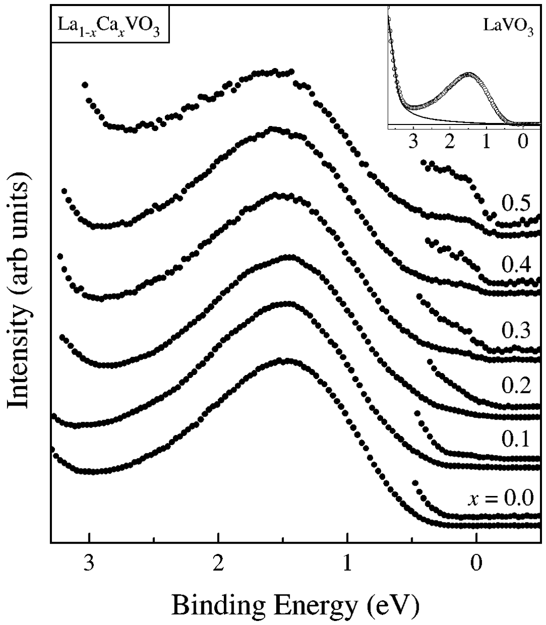

FIG. 1. He I spectra of $La_{1-x}Ca_xVO_3$. Expanded (×3) view of the near E_F region is also shown. Inset shows the expanded tailing of O p states.

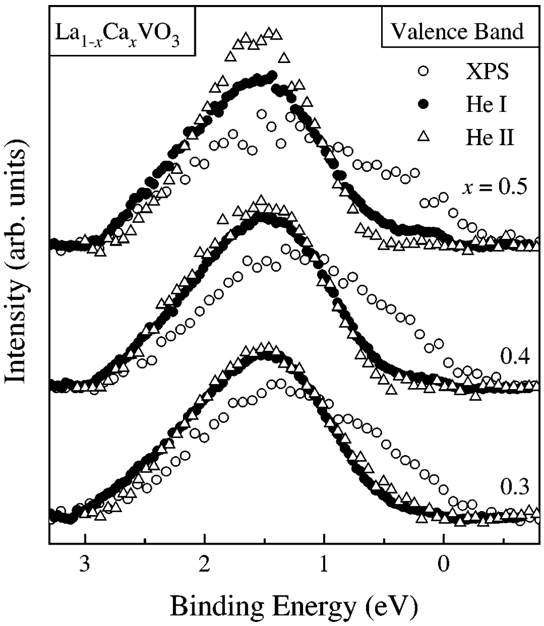

FIG. 2. Normalized (equal area) He I, He II, and XP valence band spectra of $La_{1-x}Ca_xVO_3$ for $x = 0.3$, 0.4, and 0.5.

essentially localized due to electron correlations. The spectral feature growing at E_F (coherent peak) with increasing x ($x \geq 0.2$) represents the delocalized conduction electrons. Thus, these observations show a metal-insulator (MI) transition at $x = 0.2$ in agreement with the transport properties [8]. However, the complete dominance of the incoherent feature suggests an overwhelming presence of correlation effects nearly localizing charge carriers even in the $x = 0.5$ sample, in contrast to the observed physical properties [8]. As we shall now show, at least a part of this discrepancy arises from a surface transition of the electronic structure in these systems.

The surface sensitivity of these electronic spectra can be varied by changing the exciting photon energy, since the escape depth (λ) of the electrons depends sensitively on their kinetic energy [11]. We use this fact to delineate the surface and bulk electronic structures by recording the spectra using He I (21.2 eV), He II (40.8 eV), and monochromatized Al $K\alpha$ (1486.6 eV) sources; among these the spectrum excited with He II radiation is the most surface sensitive, while the Al $K\alpha$ spectrum is expected to be the most bulk sensitive. We show the spectra for each of the metallic compositions in Fig. 2, after subtracting the O p contributions (solid line in the inset of Fig. 1) appearing at binding energies higher than 3.5 eV following the procedures in Refs. [12,13]. For each sample, the spectrum recorded with He II radiation exhibits the single incoherent spectral signature with no intensity at E_F, indicating the absence of any coherent state. This clearly demonstrates that the electronic structure in the surface region of these samples remains localized. This most probably arises from an enhanced correlation effect near the surface region due to the reduced dimensionality at the surface and/or subtle changes of surface geometry (surface reconstruction) and, consequently, a reduced bandwidth, even for the $x = 0.5$ sample. This is not entirely surprising since the critical concentration even for the bulk MI transition in the closely related, but slightly distorted, series $Y_{1-x}Ca_xVO_3$ is indeed $x = 0.5$ [14]. The finite spectral weight in the coherent feature in the He I spectrum increases further in the Al $K\alpha$ excited signal for each of the samples, consistent with an increasing bulk sensitivity of the technique. This substantiates further the view that the bulk electronic structure represents a metallic state at these compositions, though the surface layer has only localized states. Hence, to probe the true bulk spectral function, it is, however, necessary to separate the surface contribution from the total spectra in Fig. 2.

The total normalized spectral intensity F(ϵ) from the sample at normal emission is given by

$$F(\epsilon) = F^s(\epsilon)(1 - e^{-d/\lambda}) + F^b(\epsilon)e^{-d/\lambda},$$

where, $F^s(\epsilon)$ (given by the He II spectra) and $F^b(\epsilon)$ are the normalized surface and bulk spectral functions, respectively, and d is the thickness of the insulating surface layer. Expressing $e^{d/\lambda}$ as α, we readily find that $F^b(\epsilon)$ is given by $[\alpha F(\epsilon) - (\alpha - 1)F^s(\epsilon)]$. If α, which is a function of the photon energy via λ, would be known, it would be straightforward to obtain the bulk spectrum $F^b(\epsilon)$ from the above equation. In the absence of prior knowledge of α, however, we note that the spectral shape of $F^b(\epsilon)$ representing the bulk electronic structure is independent of the photon energy. Thus, the extracted $F^b(\epsilon)$ from the Al $K\alpha$ spectra must be consistent with that extracted from the He I spectrum. This consistency requirement can be cast into a least-squared-error procedure to estimate the values of

α corresponding to He I and Al $K\alpha$ photon energies. Thus, the obtained values of $\alpha_{\mathrm{HeI}} = 2.95$ and $\alpha_{\mathrm{XPS}} = 1.38$ correspond to $d/\lambda_{\mathrm{XPS}} = 0.32$ and $d/\lambda_{\mathrm{HeI}} = 1.08$, leading to a reasonable $\lambda_{\mathrm{XPS}}/\lambda_{\mathrm{HeI}} \approx 3.4$. Moreover, using the estimates of λ from the published literature [11,15,16], the present result suggests that the thickness d of the insulating surface layer is approximately 8 Å, which is roughly the dimension of the unit cell.

In inset (I) of Fig. 3 we demonstrate the subtraction procedure for obtaining the bulk spectra [17]. Thus, obtained bulk electronic structures for the metallic compositions are shown in Fig. 3 by open circles. The spectral weights show a systematic increase at E_F with increasing Ca, consistent with increasing conductivity in the series. However, the V $3d$ emission is seen to be spread to about 3 eV below E_F with the highest intensity in the vicinity of 1.5 eV. Our band structure calculations for both $\mathrm{LaVO_3}$ and $\mathrm{CaVO_3}$, however, suggest that the electronic density of states in the occupied part has a peak at E_F with a total spread of about 1 eV. Thus, it is clear that the bulk electronic structures as characterized by the spectra in Fig. 3 are strongly influenced by the electron correlation effect, leading to substantial incoherent spectral signatures giving rise to the peak near 1.5 eV and an extension of the emission down to 3 eV below E_F. The doping-dependent spectral function has been calculated within the single band Hubbard model both by dynamical mean field approximations [6] and exact diagonalization techniques [7]. These results indeed suggest the presence of the incoherent and coherent features in the spectra. However, any reasonable value of U/W with finite doping shows a much weaker contribution of the incoherent feature as compared to our experimental results. This weakened effect of correlation in the presence of large doping within a single band Hubbard model is understandable, since such doping reduces the average number of electrons per site considerably from 1.0. In the present case, there are 1.5 electrons per V site even for the highest doped case ($\mathrm{La_{0.5}Ca_{0.5}VO_3}$). In order to understand the effects of correlation in such a multiband case, we have calculated the spectral function for a degenerate Hubbard model [18], since such results are not available in the literature. We show the resolution broadened spectral functions for various values of U/W in inset (II) of Fig. 3 exhibiting a complete dominance of the coherent feature and the presence of only weak incoherent features above 1.0 eV. Thus, the inability of the Hubbard model to account for the experimentally observed intense incoherent spectral features in these doped Mott insulators [6,7] cannot be attributed to the multiband nature of the problem.

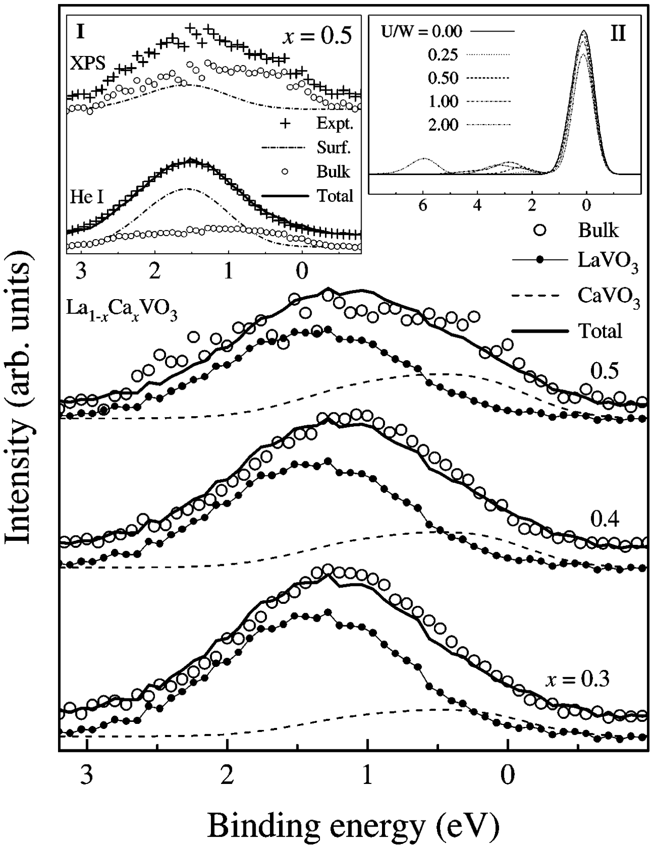

FIG. 3. Bulk spectra (open circles) of $\mathrm{La_{1-x}Ca_xVO_3}$. The solid lines show the synthesized spectra. The spectra of $\mathrm{LaVO_3}$ (solid circles) and $\mathrm{CaVO_3}$ (dashed lines) are also shown. Inset (I) shows the surface and bulk components of the spectral function for He I and XP spectra for $x = 0.5$ (see [17]). Inset (II) shows the results obtained from a multiband Hubbard model for various values of U/W.

In this context, it is important to realize that the end members of $\mathrm{La_{1-x}Ca_xVO_3}$ have fundamentally different electronic properties, one ($\mathrm{LaVO_3}$) being a Mott insulator, while the other ($\mathrm{CaVO_3}$) is a correlated metal. Moreover, we note that the peak position near 1.5 eV and its extension down to 3 eV is remarkably similar to the spectral signature of $\mathrm{LaVO_3}$ (see Fig. 3). The spectral weight shifted nearer to E_F in the metallic samples compared to $\mathrm{LaVO_3}$ is clearly the signature of the coherent feature growing in relative intensity with progressive doping of the Mott insulator. It turns out that we can model this coherent part of the spectral signature with *ab initio* band structure calculations for $\mathrm{CaVO_3}$ corrected for correlation effects within the perturbative treatment of the self-energy [19]. Considering linear combinations of the spectral features arising from $\mathrm{LaVO_3}$ and $\mathrm{CaVO_3}$, the general sum rule for the conservation of an electron number completely determines the relative contributions. This can be expressed as the total measured spectrum $\rho(\epsilon) = 2(1 - x)\rho_{\mathrm{La}}(\epsilon) + x\rho_{\mathrm{Ca}}(\epsilon)$. Here, $\rho_{\mathrm{La}}(\epsilon)$ is the normalized spectral function of the $\mathrm{LaVO_3}$ part and is completely determined from the experimental XP spectrum of $\mathrm{LaVO_3}$. x is also fixed by the composition of the compound $\mathrm{La_{1-x}Ca_xVO_3}$ and ensures a total electron count per V ion equal to $(2 - x)$. $\rho_{\mathrm{Ca}}(\epsilon)$ is calculated from the band structure results corrected up to second order in U/W. Thus, $\rho(\epsilon)$ depends on a *single* parameter U/W with all other contributions being *a priori* fixed. Noting the possible limitations of any parametric fitting procedures, we fix even the value of this parameter ($U/W = 0.5$) by requiring that the band structure results for $CaVO_3$, when corrected for correlation effects via self-energy calculation, yields the correct $m^\star/m_b = 2.1$ [20]. Thus, the calculated total spectrum $\rho(\epsilon)$ is completely devoid of any adjustable parameter. The change in the spectral features is determined solely by the value of x. The resulting $\rho(\epsilon)$ are shown in Fig. 3 by the solid lines for each of the compositions, establishing a remarkable agreement between the experiment and the parameter-free simulation. This result suggests that $LaVO_3$ and $CaVO_3$ somehow retain their characteristic electronic structures even for the intermediate compositions indicating a dominance of local interactions in determining the electronic structures; this is, however, a reasonable expectation for strongly correlated systems.

In conclusion, it is evident from our results that the surface electronic structure of early transition metal oxides can be *qualitatively* different from the bulk one. This realization is essential in order to critically discuss and evaluate the experimental electronic structure in terms of the existing many-body theories and various bulk sensitive low-energy properties. We present an algorithm to extract the bulk related spectra from the total spectra using photon energy dependent measurements. It is shown that all known theoretical results based on the single band Hubbard model [6,7], as well as the present multiband Hubbard model, are clearly insufficient to explain the experimentally observed bulk spectral functions for *any* value of U/W. It is then remarkable and significant that a simple additive description of the spectral functions of the end members, $LaVO_3$ and $CaVO_3$, though empirical and speculative, is qualitatively and quantitatively successful for all of the compositions without using any adjustable parameter and, therefore, deserves serious considerations in terms of rigorous microscopic theories for such systems. A direct consequence of this observation would be that the electronic structure of such a system is intrinsically inhomogeneous and cannot be described within a homogeneous model, such as the Hubbard model. This is in contrast to the usual practice in recent times to interpret the properties of doped Mott insulators in terms of the Hubbard model. While the presented empirical approach appears to be consistent with the spectral evolution as a function of doping of the Mott insulator, including both the coherent and the incoherent parts, it remains to be seen if, in the future, a proper theoretical model would provide a rigorous basis for understanding the physical properties of these systems.

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[17] The raw UP spectra are convoluted with Gaussians to account for different energy resolutions; normalized He I and Al $K\alpha$ spectra corresponding to $F(\epsilon)$ are represented by crosses (+) in the inset (I) of Fig. 3 while the He II spectra multiplied by $(\alpha - 1)$ (the surface component) is shown by the dot-dashed line. The resulting bulk component of the spectra is obtained from the XP spectrum by subtraction, shown as open circles. The same bulk spectrum also reproduces well (solid line) the experimental He I spectrum (the consistency requirement).
[18] The model consists of four sites with all five d orbitals and 1.5 electrons per site. The hoppings are given by Slater-Koster parametrizations with $(dd\sigma)$:$(dd\pi)$:$(dd\delta) = -2.0$:1.0:-0.2 with a total bandwidth $W = 2.4$ eV.
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